

## Effect of fillers on the fire retardancy of intumescent polypropylene compounds

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### Abstract

The effects of fillers (talc and calcium carbonate) were investigated on polypropylene /ammonium polyphosphate/polyamide-6 (PP/APP/PA-6) intumescent system by using mechanical testing, LOI method, cone calorimetry and thermoanalytical techniques. Calcium carbonate and talc affect the fire protective properties of PP/APP/PA-6 system in different ways. It is shown that talc induces an increase in the Young's modulus and a decrease in the elongation at break. Calcium carbonate leads to a decrease in the elongation at break, but there is no improvement in the Young's modulus. Talc increases fire protective performance due to forming a ceramic like protective shield at the surface, whereas calcium carbonate decreases it because of a reaction with APP. Effects of talc and calcium carbonate were furthermore investigated on PP/APP/PA-6 system by measuring Rate of Heat Release (RHR), Total Heat Emitted (THE), CO/CO<sub>2</sub> evolution and residual mass. Results are interpreted by means of decomposition, chemical reaction between components and formation of a protective shield at the surface at ignition.

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### 1. Introduction

Polypropylene (PP) represents the largest part in the polymer consumption of the world just behind the polyvinyl chloride and polyethylene. Modification of PP with fillers such as calcium carbonate or talc was earlier motivated by cost reduction. Recently however the improvement of performance becomes the main driving force of their use. The filler containing polymer compounds has numerous advantages like high modulus, excellent chemical resistance and easy processing. This is the reason why the use of polymer compounds has grown significantly in the automotive industry [1]. Incorporation of fillers in PP, however, also affects mechanical properties unfavourably. For example, the

ductility drops drastically when talc is added [2] due to stress concentrations at the interfaces [3]. In contrast the use of modified CaCO<sub>3</sub> in PP may result in an increase of the impact strength [4,5].

For safety reasons, in many applications in addition to good mechanical properties, a fire retardancy property is required. One of the promising approaches to increasing the flame retardancy whilst preserving the mechanical properties is to apply intumescent fire retardant (FR) additives [6–9]. On heating, the intumescent FR additive forms a foamed cellular charred layer on the surface of the product, which slows down the heat and mass transfer between the gas and the condensed phase [10]. In general the intumescent formulations contain three main ingredients [7], acidic source, carbonisation agent and blowing agent. Char-forming polymers can be used as carbonisation agents [11].

The incorporation of ammonium polyphosphate (APP) acid source into polyamide 6 (PA-6) charring

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polymer provides fire retardant character of interest [12]. However, because of the low compatibility of the components, the migration of the inorganic salt [13] occurs during solidification of the melt. The use of a compatibilising elastomer e.g. ethylene-vinyl-acetate (EVA) copolymer [14,15] in the intumescent PP/APP/PA6 system prevents migration and enhances flame retardancy [16]. Some authors have shown that fillers, particularly glass fibres, increased the fire retardant performance [17]. It was shown first by Bertelli et al. [18] that fillers, in particular hydrated silica or alumina, decrease the fire retardancy of APP based intumescent systems of PP. Contrary to these results, Levchik et al. [19] observed an increase in the fire properties with talc and calcium carbonate in the PA-6/APP system whereas the effect of the talc and calcium carbonate were not investigated in PP/APP/PA6 system yet.

In this study, the effect of talc and calcium carbonate on the fire retardant and mechanical properties are investigated in PP/PA-6/APP/EVA<sub>24</sub> compounds.

## 2. Experimental

### 2.1. Materials

Polypropylene homopolymer (PP) grade 3120 MN 1 (Appryl, France), MFI=8 (230 °C, 2.16 kg); Polycapromamide, polyamide-6 (PA-6), (Nyltech, France); Ammonium polyphosphate (APP), Exolit AP 462 (Clariant), (NH<sub>4</sub>PO<sub>3</sub>)<sub>n</sub>, n≈700; Ethylene vinylacetate copolymer (EVA<sub>24</sub>) EVATANE grades (Elf-Atochem, France). Commercial polypropylene-talc compound (PP-talc, or talcom), Polyfort FPP 20 T (Schulman S.A.), MFI=3 (230 °C, 2.16 kg); Talc: Fintalc M15 grade (Suommen Takki) mean size of particles = 15 µm; Calcium carbonate (Omiya, France) mean size of particles = 2.5 µm.

### 2.2. Processing and formulations

The fillers (talc and CaCO<sub>3</sub> without sizing agent) were added to PP using a Brabender DSK 42/7 intermeshing counter-rotating twin-screw extruder at 190 °C and 150 rpm to obtain a compound with mineral loading of 20 wt.%. Then the PP compounds were mixed with PA-6, APP, and EVA<sub>24</sub> using a Brabender Mixer measuring head (type 350/EH, roller blades) at 230 °C and 50 rpm, controlling of the mixing conditions using the data processing system of Brabender Plasti-Corder PL2000. The commercially available PP-talc compound was directly mixed with the other components in the mixer. Sheets (100×100×3 mm) were obtained using a Darragon pressing machine at 200 °C and at a pressure of 10<sup>6</sup> Pa. Samples were also prepared by injection moulding. The composition of the different compounds are listed in Table 1.

Table 1  
Composition of the PP based FR compounds

Label of FR compounds	Components					
	PP (wt.%)	PA-6 (wt.%)	APP (wt.%)	Talc (wt.%)	CaCO <sub>3</sub> (wt.%)	EVA <sub>24</sub> (wt.%)
Reference	60	8.75	26.25			5
PPtalcom	48	8.75	26.25	12		5
PPtalc	48	8.75	26.25	12		5
PPcarb	48	8.75	26.25		12	5

### 2.3. SEQARABIC Mechanical testing

The mechanical properties of the formulations were evaluated at 18 °C by tensile measurement using an INSTRON machine. The dimensions of the samples are as follows: useful length×width×thickness = 100×10×4 mm. Young's modulus, elongation at break are determined at a drawing speed 5 mm/min. The tested parallel samples were 10, the presented results are average data.

### 2.4. Fire testing

Limiting Oxygen Index (LOI) was measured using a Stanton Redcroft instrument on sheets (100×10×3 mm) according to ASTM 2863 [20]. UL-94 tests were carried out on 127×12.7×3 mm sheets [21].

Samples are exposed to a Stanton Redcroft Cone Calorimeter according to ASTM 1356–90 and ISO 5660 at an external heat flux of 50 kW/m<sup>2</sup>, which corresponds to the heat, evolved during a fire [22]. Conventional data (Rate of Heat Release (RHR), Total Heat Emitted (T.H.E.), CO/CO<sub>2</sub> evolutions, Volume of Smoke Production (V.S.P.) and residual mass) were computed using a software developed in our laboratory. When measured at 50 kW/m<sup>2</sup>, RHR and THE values were reproducible within the range ±10% and weight loss, CO, CO<sub>2</sub> were reproducible within the range ±15%. The presented Cone Calorimeter results are averages from three experiments.

### 2.5. Thermal analysis

Thermogravimetric analyses were carried out at heating rate 10 °C/min in a flowing synthetic air (Air Liquid grade; flow rate=5.10<sup>-7</sup> Nm<sup>3</sup>/s) using a SETARAM MTB 10-8 thermobalance. Samples of 10 mg were measured in open silica pans. The accuracy of temperature is ±1.5 °C in the range 50–850 °C.

The curves of weight difference between the experimental and theoretical TG curves are computed as follows:

$$\begin{aligned} \Delta(\text{wt}) &= \text{weight difference, } \Delta(\text{wt}) \\ &= M_{\text{exp}}(\text{wt}) - M_{\text{th}}(\text{wt}), \text{ where } M_{\text{th}}(\text{wt}) \\ &= (0.60 - X)M_{\text{poly}}(\text{wt}) + XM_{\text{fill}}(\text{wt}) \\ &\quad + 0.2625M_{\text{APP}}(\text{wt}) + 0.0875M_{\text{PA-6}}(\text{wt}) \\ &\quad + 0.05M_{\text{EVA}}(\text{wt}). \end{aligned}$$

Where  $M_{\text{poly}}(\text{wt})$ ,  $M_{\text{APP}}(\text{wt})$ ,  $M_{\text{PA-6}}(\text{wt})$ ,  $M_{\text{fill}}(\text{wt})$ ,  $M_{\text{EVA}}(\text{wt})$  are the weights of the polymer, APP, PA-6, fillers and EVA<sub>24</sub> respectively. While  $M_{\text{exp}}(\text{wt})$  and  $M_{\text{th}}(\text{wt})$  are the weight of the whole component determined experimentally and theoretically respectively. The  $\Delta(\text{wt})$  curves allow comparing to the effect of individual additives [23].

### 3. Results

#### 3.1. Mechanical properties

The stress–strain curves of compounds in Fig. 1 served for calculation of their modulus, stress and elongation at break given in Table 2. PP and intumescent FR additive system (APP/PA6/EVA) containing PP (Reference) are compared to the compounds loaded with fillers: CaCO<sub>3</sub> (PPcarb) and talc included as a pure filler (PPtalc) or as a commercial PP-talc compound (PPtacom).

Table 2 shows that the incorporation of intumescent FR additive in the PP [16], and the additional incorporation of the selected fillers leads to an increase of the

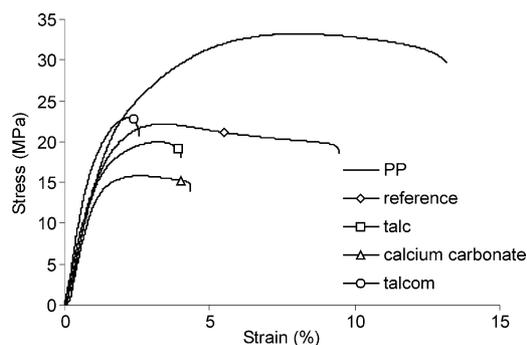


Fig. 1. Strain–stress curves of various FR formulations.

Table 2  
Mechanical properties of various FR compounds

Properties	PP	Reference	PPcarb	PPtalc	PPtacom
Young's modulus (MPa)	1340 ± 50	1730 ± 90	1750 ± 100	2200 ± 200	2400 ± 130
Stress max MPa	33 ± 1	21.8 ± 0.3	15.0 ± 0.5	19.7 ± 0.5	35 ± 0.5
Elongation at break (%)	14. ± 0.5	10 ± 0.5	4.0 ± 0.5	4.0 ± 0.5	7 ± 0.2

Young's modulus and to a decrease of the elongation at break. As expected the incorporation of the talc, especially in form of commercial PP-talc compound, gave a better performance than CaCO<sub>3</sub>.

#### 3.2. Fire testing

The LOI values and UL-94 rating data of the various FR compounds are given in Table 3. As it can be seen, the CaCO<sub>3</sub> results in a slight decrease of the flame retardancy, while the talc has insignificant effect.

The differences between the various formulations are more characteristic in the cone calorimetric RHR curves presented in the Fig. 2.

The reference compound, prepared without filler, has a typical RHR curve with two peaks, separated by a plateau [16], in which the first peak may be assigned to the development of the intumescent protective structure and the second to the degradation of this protective layer [10]. The incorporation of calcium carbonate increases the first RHR peak from 200 to 350 kW/m<sup>2</sup> and decreases the time needed for the complete degradation if compared to the reference compound.

The addition of talc in a separate step decreases the first peak of RHR but no significant differences can be observed in the value of the second RHR peak and in the time of destruction. A favourable effect can be obtained by application of the talc in the form of the commercial PP-talc compound. The stability of the protective shield, that is the beginning of the second peak, is at about 420 s, in contrast to the 300 s for the other talc-containing compound.

Further characteristics by cone calorimeter are given in Fig. 3a–d. These are the total heat evolved (THE), the CO<sub>2</sub>, the /CO emissions and the residual mass respectively. These results help to explain the influence of fillers on the burning process. The THE values in Fig. 3a do not show the differences so clearly as the RHR values in Fig. 2, however, the characteristic influence of fillers is reflected in this chart also.

The evolved CO<sub>2</sub> curves are similar for the reference and the talc containing compounds in Fig. 3b. The CaCO<sub>3</sub> containing compound shows more rapid CO<sub>2</sub> evolution, which can be the result of a reaction between the filler and the phosphoric acid formed from the APP during the combustion.

Adding talc allows increasing the delay of the CO and CO<sub>2</sub> emission compared to the blend with CaCO<sub>3</sub>. This

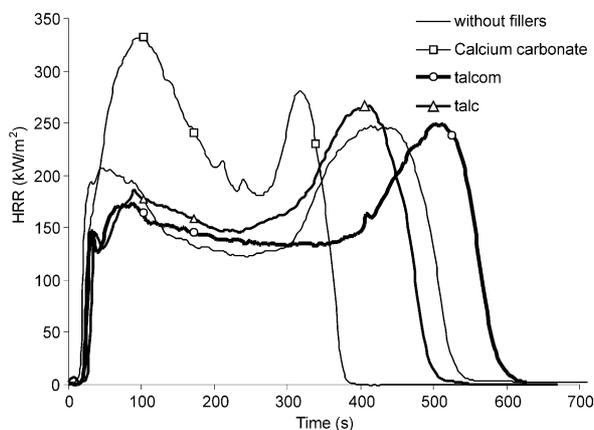


Fig. 2. The HRR versus time for PP/APP/PA6/EVA<sub>24</sub> formulations.

delay particularly increases with the commercial product and the amount of CO evolved decreases. Moreover, the amount of CO<sub>2</sub> evolved does not increase, so a part of the carbonaceous residue is preserved. Nevertheless, the efficiency of talc is reduced when the blend extruded in our lab is considered.

Table 3  
Flammability characteristics of various FR compounds

For compounds	Flammability	
	LOI (vol.%)	UL-94 rating
Reference	32±0.5	V0
Ppcarb	29±0.5	V1
Pptalc	31±0.5	V0
PPtalcom	32±0.5	V0

Using CaCO<sub>3</sub> induces a decrease in the delay to obtain the maximum value. This could be interpreted as a destabilisation of the protective shield.

The amount of the evolved CO is given in Fig. 3c. Compared to the other compounds considerable increase is caused by CaCO<sub>3</sub>, due to its induced degradation.

In Fig. 3d a higher final residual weight can be observed in talc containing compounds than in the other compounds, particularly by application of the talc in the form of commercial PP-talc compound. This phenomenon is in accordance with the higher stability.

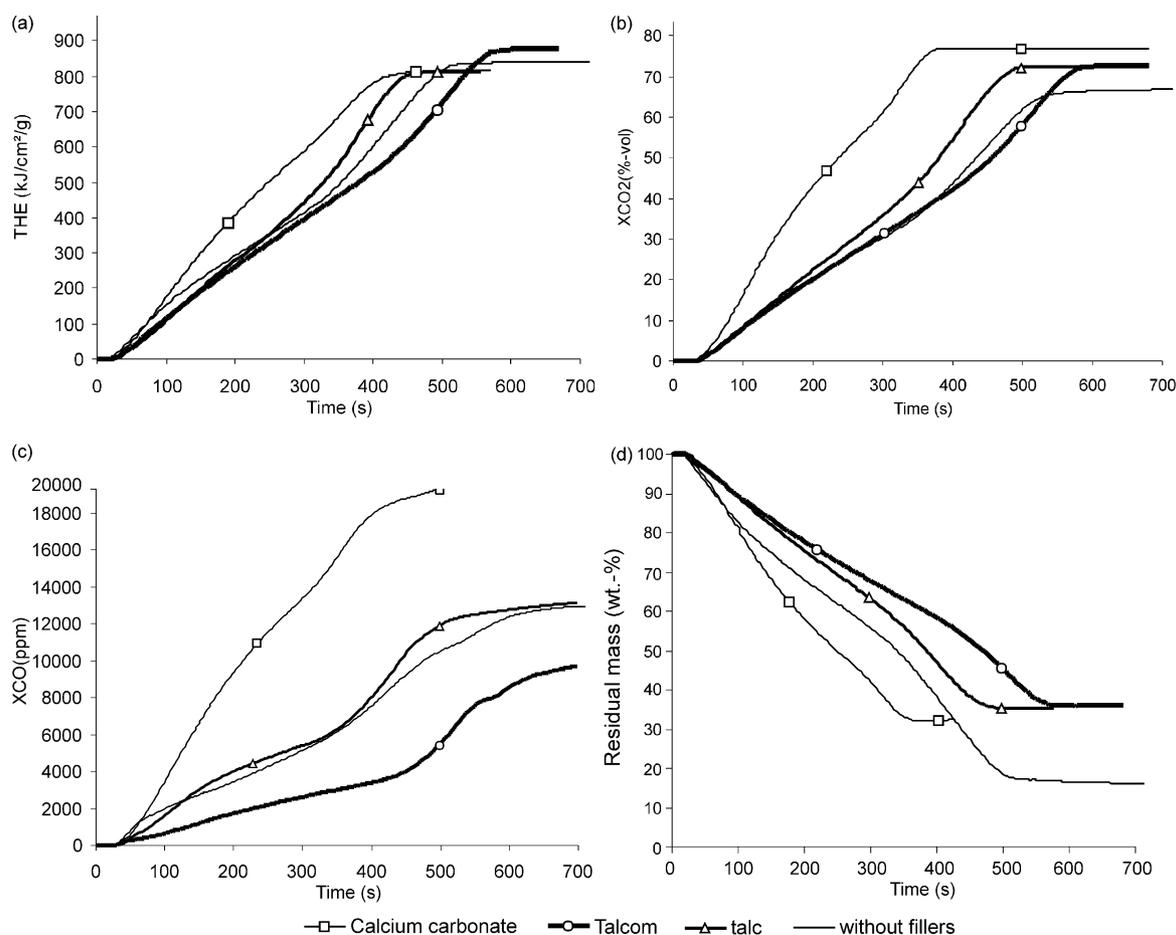


Fig. 3. Characteristic data of cone calorimetry test of PPfillers/APP/PA6/EVA<sub>24</sub> formulations; (a) THE, (b) total CO<sub>2</sub> emissions, (c) total CO emissions and (d) residual mass versus time.

Using  $\text{CaCO}_3$  leads to a loss of the thermal/fire stability in the cone calorimeter condition.

The amount of residual weight obtained is about 35 wt.% with talc and 30 wt.% with calcium carbonate whereas it is only 17 wt.% without filler. As the filler loading is 12 wt.%, some additional materials are preserved with talc in the cone calorimeter conditions.

The TG and DTG curves of the compounds are given in Figs. 4 and 5.

The TG and DTG curves of the PP/PA-6/APP/EVA<sub>24</sub> compound show four significant changes in the slopes, which proves that its degradation is at least a four main steps process. An earlier study showed that the carbonization process of the system occurs via four steps [23]. From 230 °C the additive components react with each other and form phosphate esters. Between 280 and 350 °C the development of intumescence occurs and between 350 and 430 °C the intumescent coating degrades. At higher temperatures, there are structural changes leading to the formation of new carbonaceous species (established in the temperature range  $430 < T < 560$  °C) up to 430 °C, which may be interpreted as above. Then a plateau is observed between 430 and 560 °C. This plateau may be assigned to a particular protective shield. Finally, the curve decreases at higher temperature. The carbonaceous structure is no longer protective in this stage and a “high temperature” residue is formed (about 4 wt.% at 800 °C).

The TG and DTG curves of the PPtalc/PA-6/APP/EVA<sub>24</sub> compound (Figs. 4 and 5) are similar to the curves of the compound without fillers until 560 °C. Beyond 560 °C a high temperature residue (about 32 wt.%) is obtained.

The TG and DTG curves of the PPcarb/PA-6/APP/EVA<sub>24</sub> compound (Fig. 4 and 5) show three significant changes in the slopes, which prove that its degradations is at least a three steps process. The first one begins at about 250 °C and runs until 430 °C. Then, the material shows a low rate degradation between 430 and 560 °C, and finally a high temperature residue (about 28 wt.%) is formed.

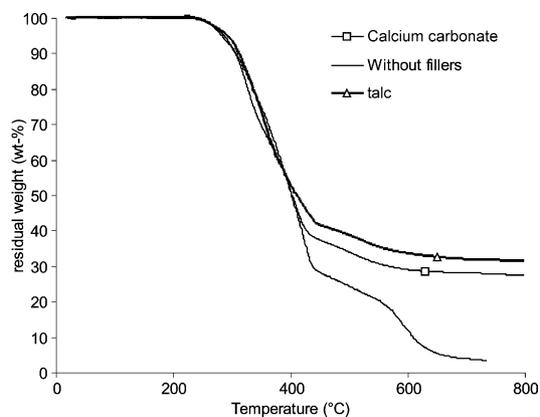


Fig. 4. TG curves of the PP/APP/PA-6/EVA<sub>24</sub> intumescent blend in air atmosphere.

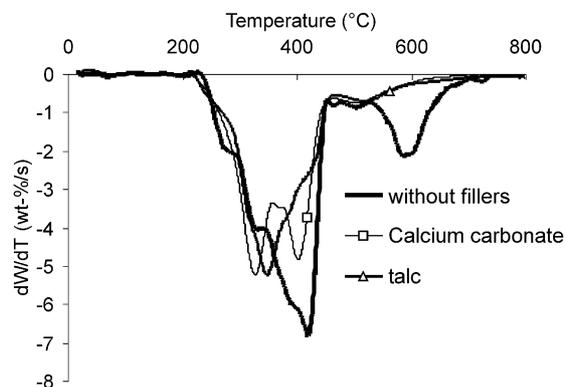


Fig. 5. DTG curves of the PP/APP/PA-6/EVA<sub>24</sub> intumescent blend in air atmosphere.

Comparing to the other compounds further differences can be noticed. The change starting at 250 °C, belonging to the interactions between PA-6 and APP in PP/PA-6/APP/EVA<sub>24</sub> and PPtalc/PA-6/APP/EVA<sub>24</sub>, is missing from the TG curve of compound with calcium carbonate. Another difference concerns the behaviour of the blends after the formation of the char. Whereas the degradation rate increases at 560 °C for the compound without fillers, it slows down with talc or calcium carbonate. Finally, the residual weight is 32 wt.% with talc, while it is only 28 wt.% with calcium carbonate.

The  $\Delta(\text{wt})$  curves are presented in Fig. 6. It is observed that the protection by the intumescence phenomenon under the conditions of thermo-oxidative degradation is a multisteps process.

In the case of PP/PA-6/APP/EVA<sub>24</sub>, the curve of weight loss difference shows that interactions between the additive and the polymeric matrix occur. The formation of the intumescent coating starts from 350 °C, which improves the stability of the system (experimental curve > simulated curve) between 350 and 500 °C. In this region ( $350 < T < 500$  °C), a coating is formed with

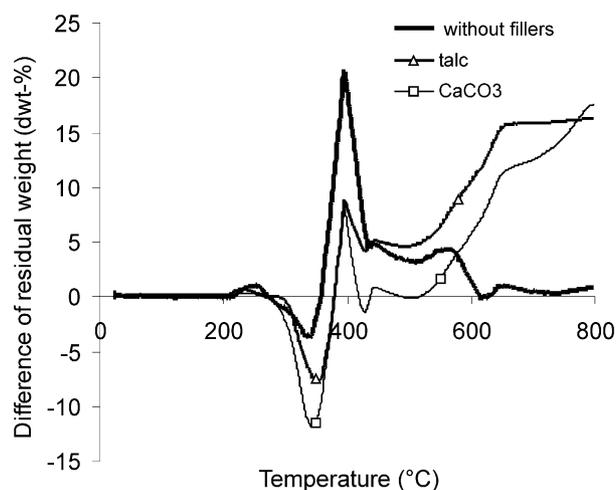


Fig. 6. Difference between experimental and theoretical TG curves of PP/PA-6/APP/EVA<sub>24</sub>, PPtalc/PA-6/APP/EVA<sub>24</sub> and PPcarb/PA-6/APP/EVA<sub>24</sub> systems (in air atmosphere).

maximal protection at 380 °C. Above this temperature, the shield gradually loses its efficiency. Above 420 °C, a second protective process is observed which leads to the formation of a second shield. Finally from 560 °C, we can assume degradation of the material (fast decrease of weight difference) and the formation of a residue.

In the case of PP/talc/PA-6/APP/EVA<sub>24</sub>, the curve of mass difference has the same shape as PP/PA-6/APP/EVA<sub>24</sub> up to 450 °C, which may be interpreted as above. Then a plateau is observed between 450 and 550 °C. This plateau may be assigned to a particular protective carbon-talc ceramic like coating. Finally the curve increases until 630 °C, when a second protective process is observed, which leads to the formation of a second shield. Then a plateau is observed at high temperature.

In the case of PP/CaCO<sub>3</sub>/PA-6/APP/EVA<sub>24</sub>, the curve of mass difference has the same shape as PP/PA-6/APP/EVA<sub>24</sub> up to 410 °C, which may be interpreted as above. Then the difference between the experimental residual weight and the computed residual weight is zero until 560 °C. There is no efficient shield which is formed as in the case of the other compounds. Over 560 °C, the curve of mass difference increases.

The comparison of the curves of mass difference shows particularly interesting results, particularly above 560 °C. The curves of the system with fillers increase whereas the curve of the compound without filler decreases. This implies that the interactions and reactions between the polymer, and the additives are larger in presence of fillers. They may form a structure which blocks polymer segments (or degradation products) in the coating and therefore, decreases the degradation rate of the system. These results are to be compared with the one observed in the case of the systems APP/PER-Zeolite in which zeolite is a synergistic agent, strongly enhancing the fire proofing performances [24–26]. The synergist acts by improving the “quality” of the intumescent coating and by “trapping” polymer segments (via the formation of stable aluminosilicophosphate esters) into the structure, improving the mechanical resistance of the shield. In our case, the formations of calcium phosphate and magnesium phosphate may act similarly.

Considering the possible formation of magnesium phosphate and calcium phosphate, due to the interaction of fillers and APP, the maximum residual weight is only about 17 wt.% for talc and 13.4 wt.% for calcium carbonate. The actual residues, however, are 32 wt.% with talc and 28 wt.% with calcium carbonate. This proves that a part of carbon is preserved at high temperature by the formation of a protective ceramic like shield.

Another point could be pointed out. As observed by TGA, the use of CaCO<sub>3</sub> reduces the delay of stabilisation.

Considering the amount of V.S.P. evolved without fillers, this is due to the combustion of a part of polymer (Fig. 7). Incorporating the fillers enable us to reduce the

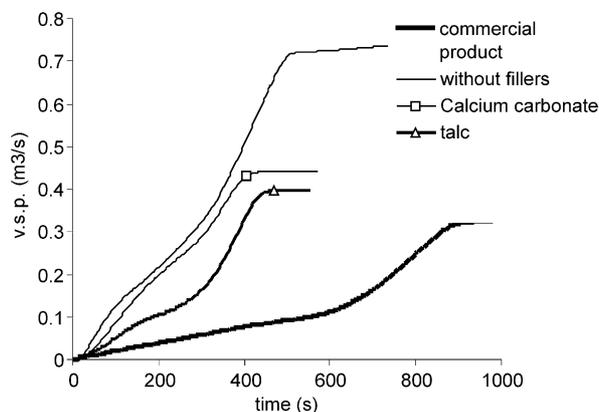


Fig. 7. V.S.P. emission versus time for PP/APP/PA6/EVA<sub>24</sub> formulations under an external heat flux of 50 kW/m<sup>2</sup>.

amount of V.S.P. increasing the conversion for a high temperature residue. Moreover, using talc enables to get a higher stability of the material which is maximal using the talc in commercially compounded form.

#### 4. Discussion

PP/APP/PA6/EVA<sub>24</sub> formulation presents enhanced fire protective performance in comparison with virgin PP. This improvement can be assigned to the formation of a carbonaceous shield during the combustion, which slows down the degradation of the formulations and which allows the formation of a stable residue [16]. With fillers, similar behaviour is observed. The fire behaviour strongly depends on the nature of the fillers.

In this work we found that the fire protective performances (decrease in the first RHR peak, increase of the residual weight). However, using calcium carbonate leads to a decrease in this behaviour. Moreover, a protective material does not form in the 420–520 °C range and the residual weight obtained (31 wt.%) is lower than with talc (36 wt.%) of the same quantities.

The results obtained with calcium carbonate could be explained by its basic character. The basic calcium carbonate reacts with APP to give calcium phosphate stable until 1400 °C [27] and the formation of phosphoric acid does not take place. Without carbonic acidic species or char former the intumescent char could not be formed as confirmed by visual observation during the cone calorimeter experiment. With CaCO<sub>3</sub>, the samples do not blow up such as with talc or without fillers. The thickness in the middle of the burning sample remains 3 mm with CaCO<sub>3</sub>, whereas, for the sample with talc it increases from 3 to 15 mm.

Thermal degradation of calcium carbonate begins at 600 °C and talc at 950 °C [28].

In the cone calorimeter condition test, the heat flux is 50 kW/m<sup>2</sup> which corresponds to a sample temperature of 630 °C. That means, the calcium carbonate degrades

in the measuring range and this could explain a lower residual weight than with talc.

Many differences were observed when talc was added separately or in the form of commercial PP-talc compound. Many reasons could explain this phenomenon, e.g. the structure of compound (crystallinity, interaction of ingredients) [1] depending strongly on the morphology and on the dimensions of the talc particles. Absence of information about the characteristics of the commercial PP-talc compound does not allow any discussion about this aspect.

## 5. Conclusion

Calcium carbonate and talc affect the fire protective properties of PP/PA-6/APP/EVA<sub>24</sub> intumescence compound in different ways. Calcium carbonate reacts with APP and removes the acid source from intumescent FR system, thus decreases its fire protective behaviour. In contrast no reaction occurs with talc and the intumescent FR effect is preserved or increased. Moreover, the residual weight of the talc containing compound, after ignition, increases and forms a ceramic like protective shield at the surface. To conclude the PPtalc/PA-6/APP/EVA<sub>24</sub> composite shows very good fire protective performance, characterised by LOI > 30 vol.%, RHR<sub>max</sub> < 250 kW/m<sup>2</sup>, a low level of CO, CO<sub>2</sub> and smoke emission which could allow its use for several applications. Furthermore some of their mechanical properties are improved compared to intumescent compound without fillers. The mechanical and fire properties depend on the characteristics of the matrix and the talc applied.

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